

An intrinsic volatility scale relevant to the Earth and Moon and the status of water in the Moon

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Abstract—The notion of a dry Moon has recently been challenged by the discovery of high water contents in lunar apatites and in melt inclusions within olivine crystals from two pyroclastic glasses. The highest and most compelling water contents were found in pyroclastic glasses that are not very common on the lunar surface. To obtain more representative constraints on the volatile content of the lunar interior, we measured the Zn content, a moderately volatile element, of mineral and rock fragments in lunar soils collected during Apollo missions. We here confirm that the Moon is significantly more depleted in Zn than the Earth. Combining Zn with existing K and Rb data on similar rocks allows us to anchor a new volatility scale based on the bond energy of nonsiderophile elements in their condensed phases. Extrapolating the volatility curve to H shows that the bulk of the lunar interior must be dry (≤ 1 ppm). This contrasts with the water content of the mantle sources of pyroclastic glasses, inferred to contain up to approximately 40 ppm water based on H₂O/Ce ratios. These observations are best reconciled if the pyroclastic glasses derive from localized water-rich heterogeneities in a dominantly dry lunar interior. We argue that, although late addition of 0.015% of a chondritic veneer to the Moon seems required to explain the abundance of platinum group elements (Day et al. 2007), the volatile content of the added material was clearly heterogeneous.

INTRODUCTION

The standard model of the lunar giant impact holds that the Moon formed when the proto-Earth was violently impacted by a Mars-sized body. Larger or smaller impactor sizes have been suggested (Canup 2012; Čuk and Stewart 2012), but the issue of how angular momentum has subsequently been removed is still under discussion. The energy released during such an impact is widely thought to have vaporized the building blocks of the Earth–Moon system. Thus, the lunar interior has long been considered to be extremely depleted in volatile elements (Wolf and Anders 1980; Papike et al. 1991; Righter 2007; Sharp et al. 2010; Elkins-Tanton and Grove 2011; Paniello et al. 2012). This notion of a dry Moon has recently been challenged

by the discovery of high water contents in lunar apatites (Boyce et al. 2010; McCubbin et al. 2010; Greenwood et al. 2011) and in melt inclusions within olivine crystals from two pyroclastic glasses (Saal et al. 2008, 2013; Hauri et al. 2011). However, these water contents were determined on pyroclastic glasses that were disseminated over large distances, but do not represent a large fraction of surface rocks and soils (Meyer et al. 1975; Butler and Meyer 1976; Hughes et al. 1988) and the consequences of such a particular emphasis deserve further attention.

The topic of water content of the Earth and its origin was addressed in the context of the planet composition in a very influential paper by Drake and Righter (2002) and is still the topic of active research and discussion (Hirschmann and Dasgupta 2009; Marty 2012). Likewise, the status of water and all other volatile elements in the Moon during and after the giant impact is poorly understood, as the volatility scales

Correction added July 12, 2014, after online publication: Table 1 was updated to a new version.

prevailing in the Solar Nebula do not apply to the composition of the Earth–Moon system. First, a lunar disk made of silicate vapor should be less reducing than the Solar Nebula, which is chiefly composed of hydrogen. Second, condensation temperatures of mineral phases also depend on the partial pressure of the elements in the cooling nebular gas and therefore on the total gas pressure (Larimer 1967). Contrary to the Solar Nebula, in which the decline in total pressure mostly reflects the declining thermal energy of noncondensable hydrogen, the gas of the lunar nebular disk is dominated by elements removed at an early stage by condensation of high-temperature phases, mostly as olivine, pyroxene, plagioclase, and metal. Overall, as argued by Righter and O’Brien (2011) and Hui et al. (2013), the uppermost water concentration of Moon should be limited to the few hundreds of ppm that would be soluble in the molten fraction at low pressures. The scales of 50% condensation temperatures T_{50} (Larimer 1967; Grossman 1972; Grossman and Larimer 1974; Wasson 1985; Lodders 2003) still widely used in the recent literature (McDonough 2003; Palme and O’Neill 2003; Albarède 2009; Wood and Halliday 2010) should therefore be replaced by a scale relevant to the Si- and O-rich gas conditions of the postimpact lunar disk (Pahlevan et al. 2011; Ward 2012).

In addition, evaluating the volatile content of both planetary objects is a challenging task (Anders 1977; Wolf and Anders 1980; O’Neill 1991) because crystal–liquid segregation during melting or magmatic differentiation as well as magmatic degassing can concentrate or dilute the absolute abundances of most elements. To see through these effects, one approach is to use the ratios of two elements that behave similarly during magmatic processes and thus provide insight into the composition of the planetary interior (Schilling et al. 1980; Hofmann and White 1983). For the purposes of this paper, we are interested in element ratios that are sensitive to volatilization during planetary accretion, but not to subsequent magmatic processes. Candidates include Rb/Ba and K/U ratios, where Rb and K are volatile and Ba and U are refractory (not volatile), but are otherwise not fractionated during magmatic processes. Thus, low Rb/Ba and K/U ratios in lunar rocks have been widely used to constrain volatile depletion in the Moon (O’Neill 1991). Zn/Fe is another element pair that is likely to be even more sensitive to volatilization. Iron is rather refractory, while Zn is volatile and its isotopes are known to be fractionated both in soils, as are many other elements, and in basalts (Moynier et al. 2006; Herzog et al. 2009; Paniello et al. 2012). Le Roux et al. (2010) used terrestrial data to show that Zn and Fe do not fractionate during basalt genesis. However, during accretionary processes, Fe is

refractory and Zn is volatile. In fact, Zn isotope fractionation by up to 2 per mil per unit mass difference in basalts is a Moon-specific feature that can be produced during the condensation of the lunar disk in the aftermath of a giant impact (Paniello et al. 2012).

SAMPLE SELECTION AND RESULTS

Here, we evaluate the Rb/Ba, K/U, and Zn/Fe composition of terrestrial and lunar mantles. For the Earth, we used fresh-glass data on midocean ridge basalts (MORB) from the PetDB database (<http://www.earthchem.org/petdb>) and ocean island basalts (OIB) from the Georoc database (<http://georoc.mpch-mainz.gwdg.de/georoc/>). For MORB, these data have been evaluated for consistency, precision, and accuracy (e.g., Albarède 2005) and the results agree with the newly produced high-precision database of O’Neill and Jenner (2012). For OIB, glasses are more uncommon, but incompatible elements are much more concentrated and we evaluated that the data are unlikely to be biased by the analytical techniques. The differences in concentration levels between the Earth and Moon are so large that potential analytical uncertainties on terrestrial samples are not relevant.

This is not the case for lunar samples, which are particularly depleted in volatile elements and for which the size of the aliquot allotted to analysts is very small. Such a restriction enhances both the blank/sample ratios and the effect of grain size on variability. One of the worst cases is for Zn, which in the Lunar Sample Compendium may vary for a same sample by two orders of magnitude (<http://curator.jsc.nasa.gov/lunar/lsc/>). For lunar basalts, we therefore gave preference to the data obtained by the more precise and accurate isotope dilution technique, or, for U, by instrumental neutron activation analysis. The isotope dilution concentration data used for the lunar samples are those from the Lyndon B. Johnson Space center (Gast et al. 1970; Hubbard and Gast 1971; Hubbard et al. 1972, 1973; Shih et al. 1975) as reported in the compilation by Wiesmann and Hubbard (1975) complemented by those from the Goddard Space Center (Schnetzler and Philpotts 1971; Philpotts et al. 1972, 1973, 1974).

It can be shown that although the abundances of each of these elements is a function of melting and/or crystallization degree, the invariance of Rb/Ba versus Ba and K/U versus K (Fig. 1) indicates that the relative abundances of these elements, e.g., their ratios, are not fractionated by magmatic processes. In agreement with previous estimates (Hofmann and White 1983), Rb in the Earth’s mantle is approximately 12 times less concentrated than Ba. Our K/U ratios are identical to

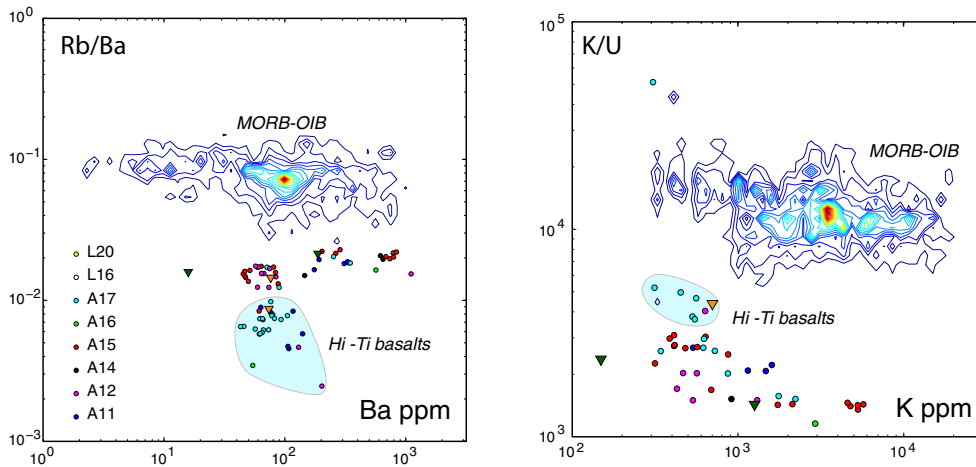


Fig. 1. *Left*. Ba and Rb are incompatible elements. Constant Rb/Ba ratios in Mid-Ocean Ridge and ocean island basalts regardless of Ba concentrations demonstrate that these two elements are not fractionated during melting and crystallization and therefore that the Rb/Ba ratio of the mantle is equal to the ratio in its melts. Data from the PetDB database and ocean island basalts (OIB) from the Georoc database. The merged 2-D histogram of MORB and OIB literature data has been contoured for clarity. See text for the source of lunar data. Rb is moderately volatile during accretion, whereas Ba is refractory. This plot shows that the Moon is depleted in Rb relative to the terrestrial mantle. Symbols refer to Apollo (A) samples. *Right*. U and K are incompatible elements. Constant K/U ratios in MORB and OIB demonstrate that these two elements are not fractionated during melting and crystallization and therefore that the K/U ratio of the mantle is equal to the ratio in its melts. K is moderately volatile during accretion, whereas U is refractory.

Jochum et al.'s (1983) terrestrial value of $K/U = 12,500$ (Gast et al. 1970; Hubbard and Gast 1971; Schnetzler and Philpotts 1971; Hubbard et al. 1972, 1973; Philpotts et al. 1972, 1973, 1974; Shih et al. 1975). We find that Rb/Ba and K/U ratios fall in a narrow range (Fig. 1). With the exception of high-Ti basalts from Apollo 11 and Apollo 17, most of the variations of the Rb/Ba ratio fall in the range 0.0125–0.02 with an average value of approximately 0.015. Likewise, most of the variations of the K/U ratio fall in the range 1500–3000, with an average value of approximately 2000 consistent with previous estimates (O'Neill 1991). High-Ti basalts have $K/U > 3000$ and $Rb/Ba < 0.01$, but their low La/Yb values point to melts from a source rich in ilmenite cumulates rather than from the average lunar mantle (Shearer et al. 2006). Rb and K are therefore depleted in the lunar mantle with respect to the Earth by a factor of 7 and 6, respectively.

Using primitive basalts and mantle peridotites, Le Roux et al. (2010) have constrained the Zn/Fe ratio of the Earth's mantle to be approximately 1.2×10^{-3} . The metal/silicate partition coefficient D_{Zn} varies with temperature from 0.5 at 1500 K to 17 at 2350 K (Ballhaus et al. 2013). The minimum value of the bulk Earth Zn/Fe ratio obtained for $D_{Zn} = 0$ is 1.4×10^{-4} . For a D_{Zn} of 17, the bulk Earth Zn/Fe ratio would be close to 1.2×10^{-3} . As alluded to above, the Zn/Fe of the lunar mantle is poorly constrained and we therefore obtained new Zn/Fe data on mineral grains (olivine and pyroxene) and glasses from basalts, pyroclastic glasses,

and igneous rocks. We simultaneously measured the concentrations of major and trace elements by laser-ablation inductively-coupled plasma mass spectrometry, following methods outlined in Le Roux et al. (2010) (Table 1). The Zn/Fe ratio of lunar basalts and minerals range between 10^{-4} and 10^{-6} and is thus 10–200 times lower than terrestrial basalts (Fig. 2). Zinc is volatile and some of it could be lost from the melt upon eruption, but the Zn/Fe values in the mesostases are consistent with those in coexisting minerals (Table 1), so this issue is at best a second-order effect. The green glass spheres have particularly heterogeneous Zn/Fe ratios. The lunar materials show a broad negative correlation between Zn/Fe and Fe content due to ilmenite fractionation, which, after about 95% of the original magma has crystallized (Hess et al. 1978), depletes Fe from the residual magma, but not Zn (the effect of the Moon's small core on Zn/Fe is negligible). Thus, the Zn/Fe of $< 6 \times 10^{-6}$ observed for the lunar basalts with the highest Fe content (Fig. 2) should be taken as representative of the lunar mantle. The Zn/Fe ratio of the Moon is therefore at least a factor 200 times lower than the value for terrestrial basalts.

DISCUSSION

Collectively, the low Rb/Ba, K/U, and Zn/Fe signatures of the Moon indicate that the Moon is more depleted in volatiles than the Earth. To relate these quantities to the water content of the lunar and

Table 1. Comparison between T_{50} (50% condensation temperature) scales and the energy of the bond of each element with a particular ligand.

| | $T_{50}L^a$ K | $T_{50}W4^b$ K | $T_{50}W6^c$ K | Bond energy ^d kJ mol ⁻¹ | Ligand |
|------------------|------------------|-------------------|-------------------|--|--------|
| H ₂ O | 182 | | | 50 | subl |
| Li | 1142 | 1225 | 1091 | 340.5 | O |
| Be | 1452 | | | 437 | O |
| CH ₄ | 40 | | | 9.1 | subl |
| NH ₃ | 123 | | | 30 | subl |
| F | 734 | | | 256 | Cl |
| Na | 958 | 970 | 821 | 270 | O |
| Mg | 1336 | 1340 | 1203 | 358.2 | O |
| Al | 1653 | 1650 | 1531 | 501.9 | O |
| SiO | 1310 | | | 454 | O |
| Si | 1310 | | | 397 | subl |
| K | 1006 | 1000 | 890 | 271.5 | O |
| Ca | 1517 | 1518 | 1382 | 402.1 | O |
| Ti | 1582 | | | 428 | subl |
| Mn | 1158 | 1190 | 1078 | 362 | O |
| Fe | 1334 | 1336 | 1183 | 407 | O |
| Cu | 1037 | 1037 | 910 | 274.5 | S |
| Zn | 726 | 660 | 605 | 224.8 | S |
| As | 1065 | | | 380 | S |
| Br | 546 | | | 194 | Br |
| Rb | 800 | 1080 | | 276 | O |
| Sr | 1464 | | | 426.3 | O |
| Zr | 1741 | | | 579 | subl |
| Rh | 1392 | | | 405 | O |
| Cd | 652 | | | 208.4 | S |
| I | 535 | | | 152 | I |
| Xe | 68 | | | 6 | Xe |
| Cs | 799 | | | 293 | O |
| La | 1578 | | | 415 | subl |
| Yb | 1487 | | | 473 | O |
| Os | 1812 | 1814 | 1666 | 575 | O |
| Ir | 1603 | 1610 | 1464 | 414 | O |
| Pt | 1408 | 1411 | 1278 | 418 | O |
| Tl | 532 | | | 161 | S |
| Pb | 727 | | | 181 | subl |
| Bi | 746 | | | 204 | Bi |
| Th | 1659 | | | 526 | subl |
| U | 1610 | | | 472 | subl |

^aLodders (2003).

^bWasson (1985) $P_{H_2} = 10^{-4}$ b.

^cWasson (1985) $P_{H_2} = 10^{-6}$ b.

^dLuo (2007) except Saxena (2007) for Cl.

terrestrial mantles requires extrapolation of these depletion factors to that of water using an appropriate intrinsic volatility scale.

Dynamics of the Protolunar Disk

To set the stage for volatile-element fractionations, some assumptions must be made about the situation in

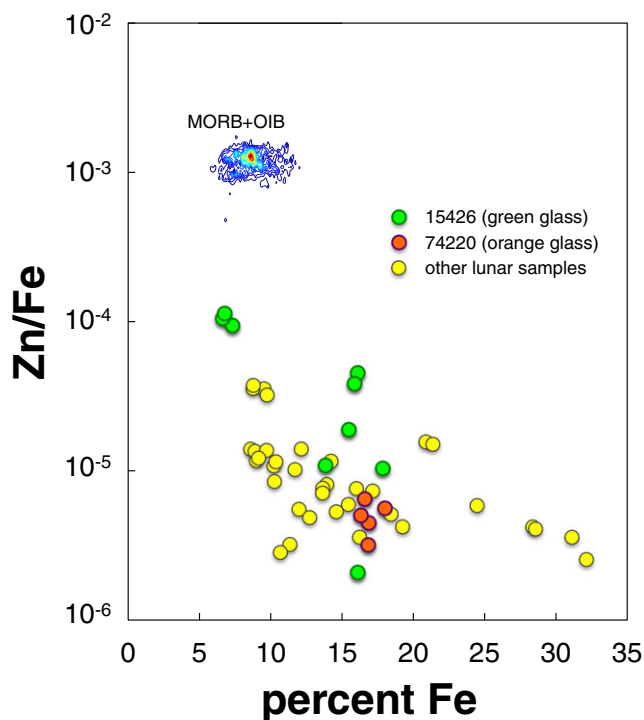


Fig. 2. Zn and Fe are compatible elements. Rather constant Zn/Fe ratios in MORB and OIB demonstrate that these two elements are not fractionated during melting and crystallization (Le Roux et al. 2010) and therefore that the Zn/Fe ratio of the mantle is equal to the ratio in its melts. Data on lunar samples are from Table 1. Zn and Fe have been measured on isolated grains of glasses, pyroxene, and olivine. The small spread of Zn/Fe ratios for a particular sample confirms that these two elements are not fractionated during crystallization. The shallow trend indicates the effect of late ilmenite crystallization in the magma ocean. The lunar mantle is depleted in volatile Zn relative to the Bulk Silicate Earth by 2–3 orders of magnitude.

the aftermath of the giant lunar impact. Temperatures rise well above 2000 K and therefore wholesale vaporization is prevalent in large fractions of the impact cloud (e.g., Canup 2004, 2012), so the collision leaves the Earth enveloped by debris, melts, and gas, which very quickly sediment in the equatorial plane of the disk. Dissipation upon interaction between the different components has two effects (Thompson and Stevenson 1988; Ward 2012). First, a rotating disk is gravitationally unstable and spiral arms form (Takeda and Ida 2001); their gravitational torque forces the condensed part of the disk to spread and a single moon quickly forms outside the Roche limit of the Earth, which is the minimum distance of about three Earth radii at which material does not break up (Ida et al. 1997; Takeda and Ida 2001; Canup 2004). Second, gas–liquid friction removes angular momentum from the condensed material, which causes the melt to drift

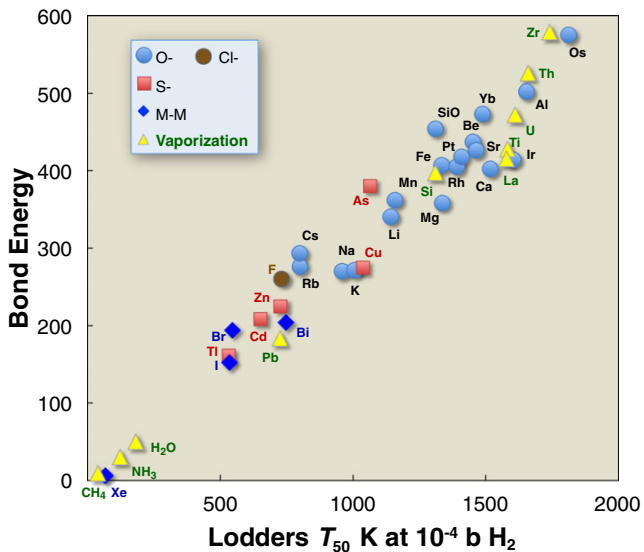


Fig. 3. Plot of Lodders's (2003) 50% condensation temperature calculated for a gas of solar composition at 10^{-4} bar versus the energy of the bonds between the element and O, S, Cl, or the element itself. Sublimation energies as indicated. Bond energies from Luo (2007).

inward and the gas to expand outward. Genda and Abe (2003) and Machida and Abe (2004) argue that, outside of the Roche limit, the Moon scattered the outer part of the disk while gas is lost by hydrodynamic escape, which explains the volatile-element depletion of the Moon. However complex this scenario may be, it is consistent with geochemical observations. The depletion of heavy Yb isotopes in the Moon relative to the Earth (Albalat et al. 2012) indicates that the refractory part of the Moon condensed out a gas-rich fraction, whereas the enrichment of heavy Zn isotopes (Paniello et al. 2012) indicates that volatile elements were lost to a large extent before condensation was complete. Although the issue of the physical status of the disk still remains to be better understood, compounded by the fact that we do not have a good grasp of the gas fraction in the disk, it is clear that a simple closed Earth–Moon system is not an adequate model.

A Volatility Scale for the Earth–Moon System

Albarède (2009) pointed out that the energy involved in most mineral and gaseous reactions is much smaller than sublimation or condensation energy. In Fig. 3, Lodders's (2003) T_{50} are plotted against the bond energy of approximately 40 elements, including most of the major elements, with O and S (Luo 2007). For Br, I, and Xe, all elements with a strong electronegativity, the energy used was that of the element–element bond. The interhalogen compound FCl was considered to limit

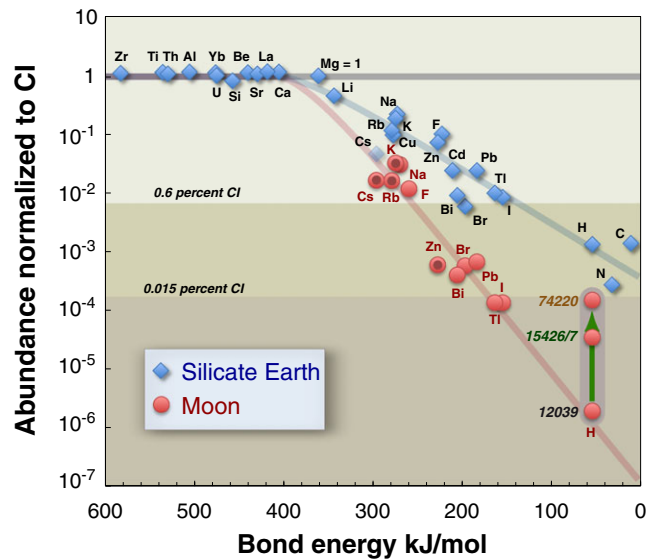


Fig. 4. Plot of elemental abundances in the bulk silicate earth (McDonough and Sun 1995) and the lunar mantle (O'Neill 1991) normalized to the Lodders (2003) CI average plotted against the bond energies of Fig. 3. Hydrogen was calculated from the $\text{H}_2\text{O}/\text{Ce}$ ratios and should be multiplied by two if seawater were to be included. Additional normalization to Mg for the Earth and to Ti for the Moon ensures that volatile loss is accounted for. Terrestrial Cs and lunar F fall off the trends. The relatively smooth trends observed for the planets provide a volatility scale that, unlike T_{50} , does not depend on the different hydrogen content of the Solar Nebula and the gas of the postimpact lunar disk. Also shown is the effect of adding 0.6% late veneer with CI composition to the Earth's primordial mantle and 0.015% CI to the Moon. The arrow shows how addition of CI chondrite to a dry mantle source typified by mare basalt 12039 may be changed into the wet sources of pyroclastic “green” glass 15426/7 and “orange” glass 74220.

the liberation of fluorine (Saxena 2007). For the most volatile components H, C, and N, which are not dissociated at very low temperatures, we used the sublimation energy of H_2O , CH_4 , and NH_3 , respectively. For the elements shown, the correlation between bond strength and volatile-element abundances is good. When the O bond energy of ultrarefractory elements, typically Ti, Th, U, Zr, and the light rare earth elements, is replaced by the sublimation enthalpy derived from vapor pressure, the elements fall back onto the main array.

It can be seen from Fig. 4 that the well-known volatility trend of the Earth and Moon (Drake and Righter 2002; McDonough 2003; Palme and O'Neill 2003) is reproduced when the bulk silicate earth composition normalized to average CI of Lodders (2003) and to Mg is plotted against bond energy. This demonstrates the applicability of bond energies as a qualitative measure of volatility independent of the composition of the vapor. The Rb, K, and Zn contents

of the lunar mantle, as inferred here from Rb/Ba, K/U, and Zn/Fe ratios of lunar basalts, define a more depleted and steeper volatile depletion curve for the Moon than the Earth. We find that elements, such as Na, F, Br, I, Cd, Tl, Pb, and Bi (O'Neill 1991), which are less well constrained for the lunar interior, also fall on the volatile depletion curve, at least within the uncertainties of their estimated abundances.

The Content of the Lunar Mantle in the Highly Volatile Elements

The coherence of so many elements on the volatile depletion curve encourages us to extrapolate to the most volatile elements, H, and to compare with measured estimates of the H content of planetary mantles. The H content of the Earth's mantle has been established using H₂O/Ce ratios of terrestrial basalts because H₂O/Ce, another volatile to refractory element ratio, is not fractionated by magmatic processes at water-undersaturated conditions due to the highly incompatible behavior (Michael 1995; Dixon et al. 2002) of both H and Ce. The H₂O/Ce is approximately 300,000 in CI chondrites (Lodders 2003) and approximately 300 in the Earth's mantle (Dixon et al. 2002). Multiplying this ratio by the Ce content of the bulk silicate earth provides an estimate of the bulk silicate earth H content, which can be seen in Fig. 4 to fall on the extension of the terrestrial volatile depletion curve to H. However, a discrepancy arises when we consider the Moon. If the lunar volatility trend is extrapolated to the bond energy of H₂O, we arrive at a bulk lunar H₂O/Ce of approximately 0.3, much lower than the terrestrial mantle (approximately 300). For a planetary Ce content of approximately 4 ppm (O'Neill 1991), this translates into a lunar water content in the subppm range, consistent with chlorine isotope evidence (Sharp et al. 2010). If, instead, we use the water contents in pyroclastic glasses (Meyer et al. 1975; Butler and Meyer 1976; Hughes et al. 1988), the orange glass 74220 (1000 ppm) and the green pyroclastic glass 15426/7 (30 ppm) (Hauri et al. 2011; Saal et al. 2013), we arrive at a different outcome. Using Ce contents of approximately 20 and 3 ppm for the orange and green glasses, respectively (Philpotts et al. 1974; Hughes et al. 1990), we find that the H₂O/Ce ratio in the mantle source of these orange and green lunar glasses must be 50 and 10, respectively. A similar ratio of approximately 10 is inferred from the Ce and pre-eruptive H₂O contents of the glassy components of soil core 74002, a sample fairly similar to the 74220 orange glass spheres (Füri et al. 2014). These higher H₂O/Ce ratios translate into approximately 120 and 40 ppm H₂O for the lunar mantle sources that gave rise to the orange and green

glasses, that is, the pyroclastic glasses imply at least 10 times higher water content in the lunar mantle than that inferred from extrapolation of volatility trends defined here by lunar mare basalts, which make up the bulk of the lunar surface soils.

An additional line of argument crucial to the discussion of water in the lunar mantle is the presence of OH-rich apatite in some lunar samples (Boyce et al. 2010; McCubbin et al. 2010; Greenwood et al. 2011). OH-bearing apatite is the ubiquitous host of terrestrial phosphate, whereas occurrence of the dry whitlockite is an exception (Ionov et al. 2006). In contrast, whitlockite, not apatite, is the common phosphate reservoir in the Moon (Jolliff et al. 1993), which is a strong indication that the interior of the Moon is largely dry. Calcium phosphate saturates only after approximately 95% crystallization (Papike et al. 1998) and we reproduced this estimate using the MELTS program (see Appendix). Typical lunar apatites contain 50% P (Friel and Goldstein 1977) and mare basalt 0.07%, so a typical mare basalt with 0.07% P₂O₅ will contain at most 0.14% apatite. A maximum bound on the amount of water can then be estimated by assuming that apatite crystals with the highest water contents were formed prior to magma degassing. The highest water content measured so far in lunar apatite is in silica-rich microgabbro 12039 (6000 ppm; Greenwood et al. 2011). First, this content accounts for 6000*0.0014 = 8 ppm of water in the magma. Second, rewriting H₂O/Ce as (H₂O/P) × (P/La) × (La/Ce) = (6000/210,000) × 31 × (2.3/5.8) = 0.35, which is a factor 1000 less than the Earth's mantle. Even if, contrary to our working assumption, large fractions of water were lost before apatite crystallization, this result does not support a particularly wet mantle source.

The simplest explanation for the discrepancy between these contrasting estimates of lunar mantle water content is that the lunar soil fragments and pyroclastic glasses sample different regions of the Moon. High-Ti basalts differ from the rest of the lunar samples with respect to their Rb/Ba and K/U ratios (Fig. 1). It has also been demonstrated that the mantle source of both the green and orange glasses had a much lower ²³⁸U/²⁰⁴Pb ratio (<50) than mare basalts (>300) (Tera and Wasserburg 1976; Tatsumoto et al. 1987), which attests to large heterogeneity of volatile distribution within the mantle even for mildly volatile elements such as Pb. Additionally, lunar mare basalts derive from a warm (1250–1350 °C) and shallow (1–2 GPa) mantle source, whereas the green pyroclastic glasses derive from unusually hot (1500–1600 °C) and deep (2–3 GPa) mantle sources (Elkins et al. 2000; Lee et al. 2009). The question is whether the lunar mantle is thus stratified in water or if the deep sources of the

pyroclastic glasses represent local water-rich heterogeneities. Given that lunar mare basalts dominate the surface of the Moon and pyroclastic glasses make up an insignificant proportion of the lunar crust, it seems likely that the essentially dry state inferred from the lunar soils is more representative of the bulk lunar mantle while the water-rich state inferred from pyroclastic glasses is a local feature. Until more water analyses on melt inclusions from mare basalts become available, the long-standing assertion that the bulk of the lunar mantle is fairly dry (Sharp et al. 2010; Elkins-Tanton and Grove 2011) remains.

The Lunar Water Conundrum

How do inferred Earth and Moon water contents fit in our current understanding of their late accretion history? The contents of platinum group elements (PGEs) and other highly siderophile elements such as Re and Au in the terrestrial mantle have been widely taken as indicating that the Earth received approximately 0.6% of a late veneer of chondrites (Chou 1978), but the actual proportion depends on what fraction of the PGE added in the process ended up in the Earth's core (Albarede et al. 2013). The PGE contents of lunar mare basalts (Day et al. 2007) suggest that the Moon received a mantle mass-normalized influx of late veneer 40 times lower than the Earth (0.015%), which would impart an H₂O/Ce ratio of 45 to the lunar mantle. Both the green and orange glasses contain a chemically separable PGE component, which points to a contribution of late accretion missing in mare basalts (Walker et al. 2004). A similar dichotomy had previously been observed for Pb isotopes (Tera and Wasserburg 1976; Tatsumoto et al. 1987). This exotic PGE component and the D/H ratios of pyroclastic glasses are consistent with a CI chondrite contaminant picked up by pyroclastic glasses just before eruption (Walker et al. 2004; Saal et al. 2013). An additional caveat was added by Gaetani et al. (2012), who demonstrated experimentally that at magmatic temperatures water diffuses in and out of melt inclusions in olivine in a matter of hours. Orange and green glasses are therefore chemical and isotopic entities of their own relative to mare basalts and cannot be considered as representing ordinary melts of the lunar mantle. For most of the rest of the lunar mantle, the late veneer material hinted at by PGEs must have been essentially dry and depleted in volatile elements.

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APPENDIX

APATITE SATURATION IN LUNAR BASALTS: CALCULATION FROM MELTS

Haskin and Warren (1991) compiled the existing data (0.045–0.18 wt% P_2O_5), but eventually recommended using a P/La ratio of 31. Both measured values and those inferred from P/La ratios suggest $P_2O_5 \sim 0.07\%$ is typical of basalts before crystallization. We used the MELTS thermodynamic modeling package to simulate the compositional evolution of a lunar basalt at 500 bar pressure. At the early stage of crystallization, olivine, pyroxene, and plagioclase are at the liquidus, while plagioclase and pyroxene (no olivine) prevail in the late stages. We treated P as a perfectly incompatible element when the system was undersaturated in apatite. Based on Watson's (1979)

experimental constraints on P content at apatite saturation, we show that apatite never saturates during batch crystallization and in the case of fractional crystallization, apatite saturates only after 96.5% crystallization when the residual melt reaches 65% SiO_2 .

SUPPORTING INFORMATION

Additional supporting information may be found in the online version of this article:

Table S1: Laser-ablation ICP-MS analyses of glass and mineral fragments. Mesostasis stands for both glassy and fine-grained multimineral fragments. The digit added to the mineral sample number refers to the fragment number, while letters identify different spots on the same fragment. For methods, standard results, and data quality, see Le Roux et al. (2010).
